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Low melting point liquid metal as a new class of phase change material: An emerging frontier in energy area

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ABSTRACT

The application of phase change materials (PCMs) grew rapidly in the last few years, especially in those areas like solar energy, thermal comfort control, green building, environmental conservation and electronic cooling etc. Tremendous efforts have therefore been made on finding new powerful PCMs or improving performance of the currently available PCMs which generally subject to inherent defects, such as low thermal conductivity, poor stability after millions of repeated solidifying and melting processes, easy phase separation during transition and narrow temperature span between the melting point and the evaporation state. To better serve for the stringent request from many emerging utilization situations, this article is dedicated to systematically present a new class of high performance PCM, the low melting point liquid metals or their alloys, which were seldom addressed before. The unique merits, application features and potential values of these highly conductive liquid like materials were summarized with their basic properties interpreted. Some latest advancement made in the area was discussed for illustration purpose. Comparative evaluation on the fundamental mechanisms and practical issues between conventional PCMs and the low melting point metal PCM was carried out. Further, some involved scientific and technical challenges were raised. The present work is expected to incubate an emerging frontier towards studying and utilizing metal PCMs in the coming time, which is rather useful for a broad range of energy areas.

Contents

1. Introduction

Facing the latest global energy and resource crisis, a new energy conservation strategy, the phase change energy storage technology (PCEST), is playing an increasing role in various

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industrial situations and daily life. The earliest PCEST was mainly used to store electricity generated from the solar energy, wind energy or ocean energy, in order to deal with the intermittent electricity generation and the frequently encountered mismatch issues in the power grids [1,2]. For these kinds of intermittent energy, electricity may be generated too much at the peak and seldom at the valley. Thus the yielded unstable voltage often cannot match with the power grid load. Fortunately, the PCM shows the ability to store abundant energy at the peak and then release it at the valley. This makes the compensation of scarce energy available. Aiming for solving such practical issues, Kenisarin and Kenisarina investigated the form-stable PCMs for thermal storage [3]. In their experiment, paraffins, fatty acids and blends, polyethylene glycol were adopted as latent heat storage component and high-density polyethylene (HDPE), styrene–butadiene–styrene (SBS) triblock copolymer, Eudragit S, Eudragit E, poly vynil chloride (PVC), poly vynil alcohol (PVA) and polyurethane block copolymer were served as structure supporting component. In another work, the authors tested the high temperature PCM in the range from 120 °C to 1000 °C which is dedicated to fulfill the use in solar thermal collector [4]. Gil et al. presented a review on the storage media systems, focusing on the storage concepts and classification, material and its property modification [5,6]. With the fast development of the PCEST, it has been extended to many other fields such as thermal management of electronic device [7], cooling of automotive engine [8], energy storage of industrial heat exchanger [9], cooling of spacecraft components [10] and thermal comfort control, such that, Rao et al. conducted an interesting experiment of using PCM as control materials to regulate the humidity in the house [11]. PCM was also integrated into the loop refrigeration and air conditioning systems so as to regulate the temperature and thus improve the overall system performance [12,13].

As is reported, buildings account for about 40% of the total world annual energy consumption and one-third of greenhouse gas emissions over the world [14]. In order to improve the energy utilization efficiency, PCEST was gradually introduced into the building area and various kinds of PCMs have been investigated [15]. The PCMs based latent heat storage is rather useful for building energy saving owing to its high storage density [16]. In such case, the PCM confined in the wall, would absorb the heat during the hot day or daytime and then release heat at a cold day or night time [17,18]. In addition, PCM has also been applied in the cooling of solar cookers [19], thermal management of Li-ion battery packs [20,21]. The finned PCM storage system has been found to work well to take advantage of the off-peak electricity tariff which will help reduce cost of the heat pump operation [22]. Further, researches also extend the application of PCM to preheating of evaporator and pressure regulator of a gaseous sequential injection system [23].

Later tremendous efforts have been made on PCM itself, which mainly involves the investigations on energy storage components [24], phase change behavior with added thermal conductivity enhancer [25,26], coupled phase change [27] and convective heat transfer [28] etc. In recent years, the research tendency regarding new phase change energy storage material, shows such a track such as transfer from inorganic to organic, from a single component to composite materials, or from macroscopic to nano/microencapsulation [29]. For example, many efforts were made on the fabrication of the microencapsulated phase change materials [30], their applications in building [31], as well as the heat transfer characteristics of microencapsulated phase change material slurry [32] etc. Overall, the PCMs of microencapsulation [33,34], technology to improve their heat transfer performance [35], applications of PCMs in building [36], thermal energy storage [37], solar energy and emerging areas have been the latest research focus [38].

PCEST utilizes the principle and phenomenon that PCM absorbs energy during melting, and then releases such heat during solidification. Meanwhile, its temperature keeps almost constant during the phase change process. PCEST was started in 1960s, and has developed from phase change principle interpretation to various categories such as utilization of specific PCMs, selection of high performance PCMs, compatibility analysis of PCMs with different container materials. For the PCEST, the PCM is the foundation of various applications. Therefore an urgent need is to find out the PCM whose latent heat is the highest per unit kilogram or per unit volume, with relatively low price and high reliability.

According to different classification mode, PCMs can be divided into categories as shown in Fig. 1. It should be noted that the solid–solid PCM does not change its state during the phase transition, but the PCM crystal type will have to vary in the process with heat absorption and release. Moreover, the solid–gas phase transition produces a large number of gases with extremely evident material volume change, leading to the fact that its phase change latent heat is the largest in such case, however seldom use of such material in the engineering situations. The liquid–gas PCMs are mainly used in heat pipe, thermosyphon, capillary pump loop, etc. In practice, the solid–liquid phase change material has a wide range of applications, especially because the commonly used hydrated salt and wax can be obtained easily.

The two main conventional classes of materials used in latent thermal energy storage systems are inorganic compounds, such as sodium sulfate decahydrate and organic compounds, such as paraffin. Organic compounds used as PCM often present some undesirable properties like: (i) low thermal conductivity, (ii) poor compatibility with the plastic container and (iii) moderate flammability. The major problem in using inorganic compound as PCM is its stability. For example, melted crystal water of sodium sulfate decahydrate is easy to evaporate during working. The solid salt, due to its higher density, settles down at the bottom of the container and is unavailable for recombination with water during the reverse process of freezing. This results in an irreversible melting–freezing of sodium sulfate decahydrate. Another important problem common to sodium sulfate decahydrate lies in the supercooling behavior. At the fusion temperature, the nucleation rate is generally very low. To achieve a reasonable nucleation, the solution has to be supercooled and hence energy is discharged at much lower temperature instead of fusion point. Other problem occurred on sodium sulfate decahydrate is the spontaneous salt hydrates with lower number of water moles during the discharge process such as sodium sulfate heptahydrate. Both the inorganic compounds and organic compounds have extraordinary small thermal conductivity.

Overall, the common shortcoming of many potential phase change heat storage material is their low thermal conductivity, which falls between 0.15 and 0.3 W/(m °C) for organic materials and between 0.4 and 0.7 W(m °C) for salt hydrates [39]. This results in poor heat exchange between the heat transfer fluid and the storage material. Therefore, tremendous efforts were made in recent years to improve the thermal conductivity of PCMs. Typical approaches are found as adding highly conductive foam copper, aluminum or copper fin into paraffin wax, or loading expanded graphite particle into PCMs, etc. [40]. A review by Fan and Khodadadi [41] summarized the recent progress in enhancing the thermal conductivity of the PCM, which was used in the thermal management of the aeronautics electronics and storage of solar thermal energy. The focus was paid on the techniques such as mixed PCM and graphene, stationary high conductivity inserts/structures, added fins or carbon nanotube [42]. Generally, copper, aluminum, nickel, stainless steel and carbon fiber in various forms (fins, honeycomb, wool, brush, etc.) were adopted to improve the thermal conductivity of the PCM.

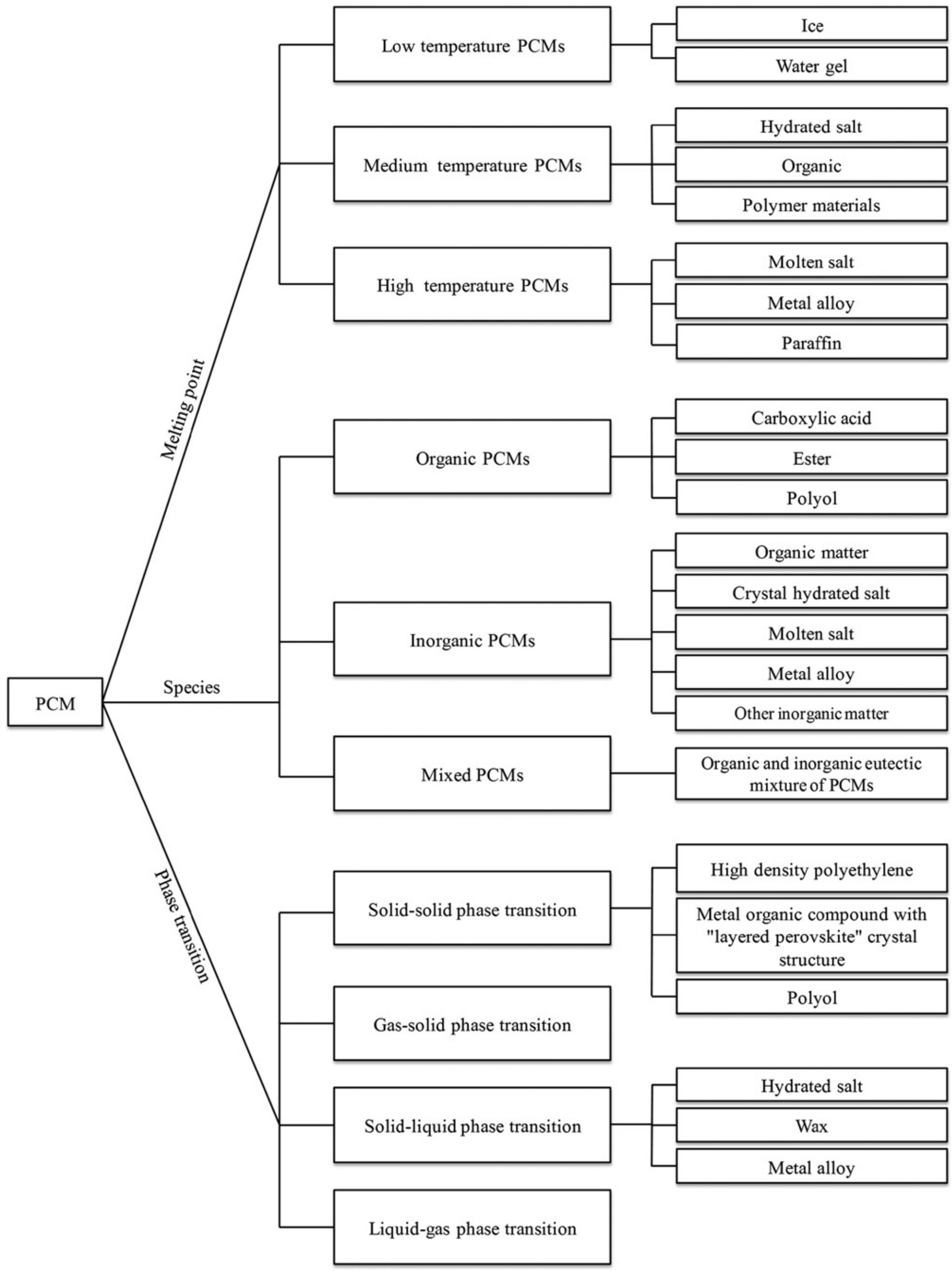


Fig. 1. Category of PCM based on melting point, species, and phase transition mechanism.

Meanwhile, serious issues also occur if only focusing on the conventional PCMs. For example, compositing a highly conductive material has often been a tough processing technique, and is difficult to handle. It is based on the above fact, we believe that an alternative game changing strategy towards innovating the PCEST should be taken. Clearly, a most efficient way to improve the thermal conductivity of the PCM is to directly adopt materials with high thermal conductivity which however could transit easily from solid state to liquid phase or vice versa so as to quickly absorb or release heat. In this side, one of the most promising answers comes to the low melting point metal or alloy. Such material was recently introduced into the areas like thermal management of computer chips [43], harvesting low grade heat to generate electricity [44,45], as well as cooling of high power LED [46], etc. And its unique roles to tackle many important related issues are also increasing such that in spacecraft thermal management [47]. Starting from this consideration, we are dedicated here to systematically propose a new frontier of investigating the low melting point metal or its alloy as a powerful PCM. Its application in tackling a series of tough energy or thermal management issues will be illustrated. The related technological challenges and scientific issues will be digested.

2. Basic features of low melting point liquid metals as PCMs

2.1. Selection criterion of PCMs

In the late 80s, the U.S. Dow chemical company has tested nearly 20,000 kinds of PCMs and the results showed that only 1% of them can be of practical value, which mainly attribute to the melting salt hydrate and part of the organic PCMs. Due to the economic and technical restrictions, suitable PCMs for storage building materials and solar energy is even less. Generally, an

ideal PCM used for low energy consumption should meet the following requirements [48,49]:

(1) the melting point of the PCMs must match with the application situation, i.e. the melting point lies in the working temperature of the device;
(2) the material should have large enough phase change latent heat to absorb as much as possible thermal energy;
(3) the PCM owns relatively small phase expansion to make sure the system work safely;
(4) the material has excellent reversibility of phase transition;
(5) the PCM should be of non-toxic, non-corrosive and produce no chemical reaction to the container and devices;
(6) the raw material is cheap and could be easily available.

But in fact, PCMs which can perfectly satisfy all the above conditions do not exist. Therefore many technical solutions were proposed to improve the performance with typical ways like:

(1) obtaining PCM compounds from binary or multiple PCMs, such as organic and inorganic compounds, which produce the right phase transition temperature and phase change latent heat [50];
(2) keeping the shape of the solid–liquid PCMs. The main component of such PCMs includes: work material and carrier substrate. The former is used to store energy or absorb heat; the latter is to confine the PCMs inside, and the carrier generally owns higher phase transition temperature. The carrier must be compatible with PCM, no corrosion, no chemical reaction and low cost, etc. [51,52];
(3) in order to enhance the thermal conductivity of the most non-metal PCM, it becomes necessary to add some high thermal conductivity material (such as aluminums or copper), which are known as heat conduction enhancers. Also some other thermal conductivity enhancer methods were proposed [53,54];
(4) in order to reduce the degree of supercooling, homologous nucleating agents or impurities were added to the PCM [55–57];
(5) the problem of incongruent melting can be tackled by one of the following approaches: (i) Mechanical stirring; (ii) encapsulating the PCM to reduce separation [58,59], (iii) loading of the thickening agents which prevent setting of the solid salts by holding it in suspension [60], (iv) use of excess of water so that melted crystals do not produce supersaturated solution [61], (v) modifying the chemical composition of the system and making incongruent material congruent [62,63].

2.2. Basic features of low melting point liquid metals

Metals have giant atomic structures held together by metallic bonds. Former researches have found that in addition to the rearrangement of sodium atoms in liquid under pressure, electrons are transformed as well. The electronic cloud gets modified, and the electrons sometimes get trapped in interstitial voids of the liquid, and atomic bonds adopt specific directions. As is well known, the metallic bonds between metals atomics were the strongest. Thus the energy needed to destroy the metallic bonds and finally lead to phase transition from solid to liquid was larger than other non-metallic PCM.

The thermal conductivity of the metal caused by the electron motion is much higher than that of the general liquid contributed by molecular movement, such as water, oil, and many organic fluids. Thus, if certain metal (or its alloys) with a low melting point is adopted as a PCM, a much stronger heat transfer capacity than that of traditional fluids can be obtained. Starting from this basic point, the present authors' lab introduced the low melting point metals or their alloys as PCM for the thermal management of a group of mobile electronics such as USB flash memory or smart phone. Similarly, low melting point metals should also work well as a potential PCM candidate for next generation industrial heat exchangers because of their many favorable properties, such as high thermal conductivity, good electrical conductivity, low vapor pressure, small volume expansion during the phase transition. Meanwhile, such material generally owns pretty high boiling point above 2000 °C, and large volumetric latent heat of phase change.

To summarize, several typical thermo-physical properties of metal or alloy used as PCM were listed in Table 1. It can be observed that the temperature gap between the melting

Table 1
Thermo-physical properties of typical metals or alloys with low melting point [64,65].

Liquid metals	Melting point (°C)	Evaporation point (°C)	Specific heat (kJ/(kg °C))	Density (kg/m^3)	Thermal conductivity (W/(m °C))	Enthalpy of fusion (kJ/kg)
Mercury	−38.87	356.65	0.139[a]	13 546[a]	8.34[a]	11.4[a]
Cesium	28.65	2023.84	0.236[d]	1796[d]	17.4[d]	16.4[d]
Gallium	29.8	2204.8	0.37[n]	5907[n]	29.4[n]	80.12[n]
Rubidium	38.85	685.73	0.363[m]	1470[m]	29.3[m]	25.74
$Bi_{44.7}Pb_{22.6}In_{19.1}Sn_{8.3}Cd_{5.3}$	47	–	0.197	9160	15	36.8
$Bi_{49}In_{21}Pb_{18}Sn_{12}$	58	–	0.201	9010	10	28.9
Potassium	63.2	756.5	0.78[m]	664[m]	54.0[m]	59.59[d]
$Bi_{50}Pb_{26.7}Sn_{13.3}Cd_{10}$	70	–	0.184	9580	18	39.8
$Bi_{52}Pb_{30}Sn_{18}$	96	–	0.167	9600	24	34.7
Sodium	97.83	881.4	1.38[d]	926.9[d]	86.9[d]	113.23[d]
$Bi_{58}Sn_{42}$	138	–	0.201	8560	19	44.8
Indium	156.8	2023.8	0.23	7030[c]	36.4[c]	28.59[m]
Lithium	186	1342.3	4.389[b]	515[b]	41.3[b]	433.78[b]
$Sn_{91}Zn_9$	199	–	0.272	7270	61	32.5
Tin	232	2622.8	0.221	730[d]	15.08[b]	60.5[m]
Bismuth	271.4	1560	0.122	979	8.1	53.3

[a] At 25 °C.
[b] At 200 °C.
[c] At 160 °C.
[d] At 100 °C.
[n] At 50 °C.
[m] At melting point.

Table 2
Metal PCM category.

Category	High temperature	Middle temperature	Low temperature
Temperature scale	Above 200 °C	40–200 °C	0–30 °C
Typical metal PCM	Other metal alloy	Bi-based metal alloy	Ga-based metal alloy
Application	Solar energy	Wasted heat recovery and solar energy	Thermal management, building energy conservation and thermal comfort

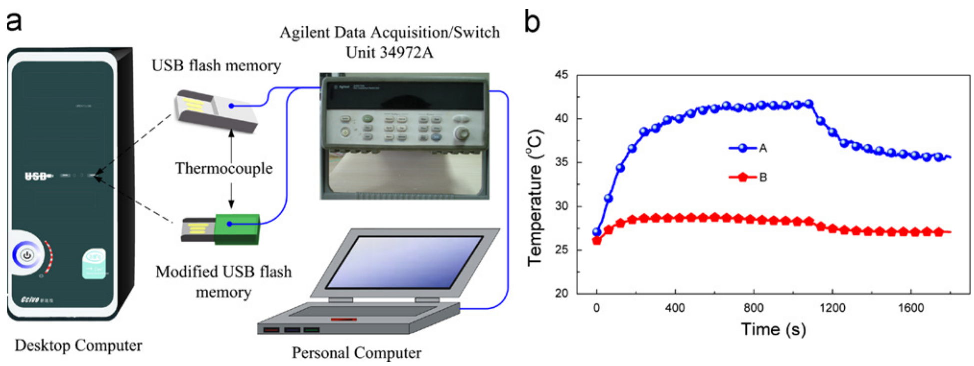


Fig. 2. Gallium PCM based thermal management of USB flash memory. (a) Schematic of the experimental setup; (b) Test results: Curve *A* indicates temperature of the original USB flash memory and curve *B* is for the modified USB flash memory filled with gallium PCM. During the test, 3.6 G data file was copied from the desktop computer to the USB flash memory; and the ambient temperature was around 24 °C. (with permission from Ge and Liu [67]).

temperature and evaporation point of metal was extremely large. This guarantees the rather wide suitability of such kind of PCM in many fields.

Different from the routine approaches, using metals as PCM can efficiently solve the problems emerged in traditional PCMs, owing to their super thermo-physical property. Classified by melting point, metal PCM can generally be divided into three categories, high temperature, middle temperature and low temperature as listed in Table 2. Their application fields are also provided in the table.

2.3. Low melting point liquid metal used as PCM

It should be pointed out that, the low melting temperature metal or alloy was seldom used before as PCM. Among the rather limited efforts ever tried, Chi et al. investigated the role of using gallium-based alloy for the cooling of a laser system [66]. Their result indicates that under the vacuum condition and the surrounding temperature 25 °C, the gallium-based PCM cooling system could maintain the optical mirror of the laser system below 40 °C, which would well confine its thermal distortion.

Another area which the low melting point metal PCM would play important roles is in consumer electronics. As demonstrated in our lab [67], the instantaneous heat generated from the USB flash memory during transferring big data could be well absorbed by the gallium PCM filled inside. For a typical commercially available flash memory, only about 0.668 mL gallium PCM will be enough to maintain its temperature below 29 °C for more than 18 min. This is sufficient to guarantee the safe running of the data device. Compared with the conventional USB which may quickly come up to above 42 °C, the temperature of the gallium cooled USB was dramatically reduced Fig. 2.

Further, we also extended the application of low melting point metal PCM to more situations, such as thermal management of mobile phone or panel personal computer where transient high heat generation is often released [68]. In the experiments and theoretical analysis to evaluate the capacity of the new method, a heating chip was used to simulate the smartphone and cooled by an attched stainless steel container filled with gallium PCM. For comparison purpose, three kinds of conventional PCMs such as

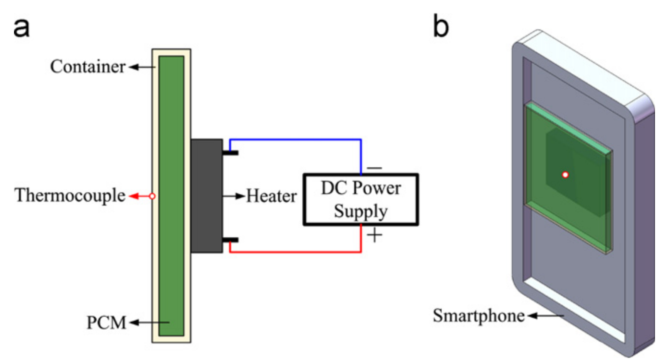


Fig. 3. Gallium PCM based thermal management of smartphone. (a) Schematic for the experimental setup and (b) isometric view of the container adhered to the smartphone.

sodium sulfate decahydrate, paraffin, N-eicosane and gallium were filled in the container, respectively. According to the measurement, it was found that under the same heating power, the entire time for keeping the container temperature below 45 °C was about 300 s for the case with nothing filled inside, 500 s for paraffin case, 600 s for N-eicosane case, and 800 s for sodium sulfate decahydrate case. While for the gallium cooled case, the maintaining time is 1000 s. Clearly, such performance over conventional PCMs is rather evident. The work suggests the unique values of the metal PCMs in a variety of thermal management areas which request instanteous heat absorption (Fig. 3).

Overall, the significant advantage of metal PCM lies in its large latent heat of melting which provides high energy storage density. The latent heat should be as high as possible, especially on a volumetric basis, so as to minimize the physical size of the modular and cooling system. When a solid metal PCM melts, phase change occurs. The transition from solid state to liquid state allows large amounts of energy to be absorbed in metal PCM. Even latent heat is stored inside the PCM, the temperature however remains fairly constant with very small volume changes. Only until the phase change is finished, the temperature will increase as heat is applied. But if the heating is ceased, the temperature would decrease due to natural cooling.

3. Important energy areas of low melting point liquid metal

3.1. PCM used in solar energy

Solar energy is free, environmentally clean, and widely available. Therefore, it is recognized as one of the most promising alternative energy recourses options. In the near future, the large-scale utilization of solar energy for various applications, like cooking, heating, cooling and drying, can be anticipated. However, as is well known, solar energy is intermittent and instable, leading to the mismatch between the supply and demand of energy. Hence, a lot of technical and economic problems have to be solved before large-scale utilization of solar energy. Thermal energy storage remains among the top ranks of these problems, especially when talking about long-term storage [69]. Thermal energy can be stored as sensible heat (water and rock), latent heat (water/ice and salt hydrates), heat of reaction, or combination of them. Parameters including storage period required, economic viability or operating conditions are important for selection of these strategies [70]. In terms of storage media, a wide variety of choices exists depending on the temperature range and application process. PCMs offer many advantages such as high storage density and small temperature fluctuation, allowing their application to be one of prospective solar energy techniques.

Since Sokolov and Keizman firstly presented PCM in a solar collector [71], there have been many studies along this way. A large number of PCMs (organic, inorganic and eutectic) are available in any required temperature range from 0 °C to 150 °C that is interesting for solar applications. The commonly used PCMs in solar thermal energy storage are fatty acids, paraffins, and hydrates. Fatty acids have always aroused interests among researchers as a feasible potential PCM. This is due to their low toxicity, melting congruency and better chemical stability [72]. Commercial paraffins and paraffin waxes are more attractive for application in solar heating systems since they are produced in large quantities and widely used elsewhere with low corrosion and chemical stability [39,73]. Hydrates are handy and have proper melting point, but suffer from the relatively high degree of supercooling and poor chemical instability once heated, making their application rather limited. Furthermore, it should be noted that sugar alcohols such as erythritol and mannitol have a phase-change point of over 100 °C. Recently, erythritol with a melting point of 118–119 °C has been reported as a promising new PCM for applications in solar cookers [74,75]. Table 3 shows data on some materials which can be used only in solar applications and presented thermo-physical properties that closely match numbers from data for pure salt hydrates.

On the other hand, high temperature PCMs with melting temperatures above 300 °C have the potential for thermal energy storage in concentrated solar power plants [76]. They include pure salts, salt eutectics, metals and metal eutectics. Among them, the PCMs having melting temperatures in the range of 300–550 °C can be potentially employed as energy storage media for solar power plants with currently available heat transfer fluids (HTFs) (oils, water/steam and molten salts) [77], although so far no commercial high temperature PCM technology is available. All the storage materials used currently in solar power plants are based on liquid sensible heat storage [78].

The use of molten salts as thermal storage media allows for high storage temperatures range of 450–500 °C with very low vapor pressures, thereby reducing the volume of the thermal storage unit for a given storage capacity [79]. Moreover, molten salts are liquid at atmospheric pressure, providing an efficient, low cost medium in which to store thermal energy. Their operating temperatures are compatible with today's high pressure and high-temperature steam turbines [80]. And such materials are non-flammable and non-toxic, more environmentally friendly than currently available high-temperature oils. Up to date, the most often used molten salts are Hitec, Hitec XL and the so-called solar salt, and the range of temperatures at which solar salt may work has been proven in solar thermal power plants (STPPs) like Solar Two or Andasol I [79,81]. Their thermo-physical properties are listed in Table 4 [82]. However, the major challenge of the molten salt is their relatively high freezing temperature (120–220 °C), which means that special attention has to be dedicated to freeze protection operation in the solar field, such as the use of fossil fuels or electric heating during the night or in poor weather conditions, thus increases operation and maintenance requirements. To overcome these problems, new salt mixtures are being investigated and developed. For instance, new salt mixtures with the potential for freezing points below 100 °C (beyond 100 °C the freezing problem is expected to be more manageable) are being developed in Sandia National Laboratories [78]. On the other hand, molten salts as PCM for high temperature application suffer from low thermal conductivity in general, which leads to slow charging and discharging rates [83]. For enhancing heat exchange rate, cost-effective fabrication of PCM composites [53,84,85] and PCM capsules [86–88] having high thermal conductivity are strongly required.

Table 3
Thermo-physical properties of some phase change heat storage products from EPS Ltd [39].

Trade mark	Melting point (°C)	Heat of fusion (kJ/kg)	Specific heat (kJ/(kg °C))	Heat conductivity (W/(m °C))	Density (kg/l)	Volume expansion [a] (%)	Heat storage capacity (kWh/m^3)
E21	21	150	0.68	0.43	1.48	8–9	32.4
E23	23	155	0.69	0.43	1.475	8–9	33.3
E28	28	193	2.22	0.21	0.769	8–9	28.2
E30	30	201	0.69	0.48	1.304	8–9	38.3
E32	32	186	0.78	0.51	1.460	8–9	39.8
A32	32	145	2.20	0.21	0.845	9–10	26.6
E44	44	105	1.61	0.43	1.584	8–9	24.3
E48	48	201	0.70	0.45	1.670	8–9	49.1
E50	50	104	1.59	0.43	1.601	8–9	24.4
E58	58	167	2.55	0.69	1.505	8–9	36.7
E71	71	123	1.86	0.51	1.690	8–9	30.4
E72	72	140	2.13	0.58	1.666	8–9	34.0
E83	83	152	2.31	0.62	1.600	8–9	35.5
E89	89	163	2.48	0.67	1.550	8–9	37.0
E117	117	169	2.61	0.70	1.450	8–9	35.8
A164	164	306			1.500	9–10	67.1

An Authors evaluation; E—materials on the bases of salt hydrates; A—materials on the basis of alkane/aliphatic solutions.

Besides the high freezing points and low thermal conductivity of the molten salts, their serious corrosion and large volume changes during melting also limit the applications. Metals that could diminish these problems are quite competitive despite the lower density of the heat storage. Metal and metal alloys have many advantages, such as high thermal conductivity, low corrosion activity and small volume change during melting/freezing [77]. Furthermore, they have a small latent heat based on the weight, but a large latent heat based on the volume. This implies that they are suitable for energy storage at the same location but unsuitable for energy transportation [89]. Several metallic materials have been proposed as PCMs with high phase change points [90,91] for applications in solar power generation systems. However, the low melting point metals and metal eutectics have not yet been seriously considered for PCM technology. A list of some selected metals is given in Table 5.

The thermal storage of solar energy can be considered as one of the most prospective applications for low melting point metal based PCMs. And the solar thermal energy storage systems combined with PCMs will be able to be used efficiently and widely in practical situations when PCMs have the longer using life, the lower cost and improved performance by technological improvements. Higher operation temperatures are achievable and higher storage temperatures (above 550 °C) may be required in the future. Thus, metals and metal alloys with higher melting point could also be utilized.

Table 4
Characteristics of the nitrate salts [82].

Property	Solar salt	Hitec	Hitec XL (calcium nitrate salt)
Composition, %			
$NaNO_3$	60	7	7
KNO_3	40	53	45
$NaNO_2$		40	
$Ca(NO_3)_2$			48
Freezing point, (°C)	220	142	120
Upper temperature, (°C)	600	535	500
Density @ 300 °C, (kg/m^3)	1899	1640	1992
Viscosity @ 300 °C, (cp)	3.26	3.16	6.37
Heat capacity @ 300 °C, (J/(kg °C))	1495	1560	1447

Table 5
Melting point and latent heat of fusion of metals [48,92].

Material	Melting point (°C)	Latent heat (kJ/kg)	Group[a]
Gallium	30.0	80.3	I
Cerrolow eutectic	58	90.9	–
Bi-Cd-In eutectic	61	25	–
Cerrobend eutectic	70	32.6	I
Bi–Pb–In eutectic	70	29	–
Bi-In eutectic	72	25	–
Bi–Pb–tin eutectic	96	–	–

[a] Group I, most promising; and, insufficient data.

3.2. PCM used in thermal comfort maintenance

Thermal comfort is generally defined as that the condition of the human mind which expresses satisfaction with the thermal environment. With the help of thermal equations designed to predict thermal comfort, thermal comfort charts and thermal indices have already been developed. The thermal comfort feeling of the human body is always influenced by a variety of parameters. Among those, the three main factors are: environmental climate, clothing, and physical activity [93]. Except for physical activity, clothing is the only factor that can be easily changed by human beings, i.e. wearing thick clothes in winter while wearing thin clothes in summer. It is known that PCMs possess the ability to change their state within a certain temperature range. Let us take liquid–solid PCM as an example. When temperature rises during the heating process, the PCM absorbs heat and stores this energy in the liquefied PCMs, as phase change takes place. When the temperature falls again, the PCM releases this stored thermal energy and the PCM solidifies again, which will act as a reverse cooling process. Therefore, a PCM has two types of thermal effects: one is a cooling effect by absorbing heat when it melts and the other is a heating effect due to heat release when it solidifies.

Many studies were conducted to apply PCM in thermal comfort field. Such materials have already been adopted as building materials to regulate an entire built environment [94], as mentioned before. However, this application requires a large consumption of energy and materials. A much more energy and material saving alternative is to use PCMs in clothing or textiles to improve the micro-climate around human torso. It has been proven that incorporating PCM microcapsules into textile structure can change and improve its thermal performance, which would provide comfortable temperature for human body [95]. Thus, textiles with PCM will help avoid extreme temperatures, through absorbing and releasing large quantity of latent heat in narrow temperature band of phase change.

Nowadays, in addition to water, there are more than 500 natural and synthetic kinds of PCMs available. Among them, only a few possess the properties that could be used in thermal comfort field. Some of these PCMs are listed in Table 6, which have different types of transition, phase change temperature ranges, latent heat, and densities. PCMs for thermal comfort field should react to changes in temperature of both the body and the outer layer of the garment when they are applied in the textile substrate. Thus, a phase change within the ambient temperature and comfort range of humans are suitable, i.e. in a temperature range from 18 °C to 35 °C. The required properties for a PCM for thermal comfort areas [96] are listed as follows: (a) melting point

Table 6
PCM candidates applied in thermal comfort field [92].

Material type	Type of transition	Phase change temperature range(°C)	Latent heat (J/ml)	Density (g/ml)	Examples
Organic compounds	Solid–liquid	−12–187	125–400	0.75–1.54	Paraffin, *n*-alkenes, mixture, fatty acids, alcohols, sugars,
Hydrated inorganic salt	Solid–liquid	20–140	270–650	1.5–2.2	$Na_3SO_4 \cdot 10H_2O$ $Cacl_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$ $MgSO_4 \cdot 7H_2O$,
Inorganic salt	Solid–liquid	< 150	200–500	1.7–2.5	$LiNO_3$, $NaNO_3$, $Mgcl_2$, K_2CO_3
Solid–solid organic compounds	Solid–solid	21–100	140–200	1–1.1	TCC
Metal eutectics	Solid–liquid	30–25	200–800	6–10	Eutectics of Bi–Pb–Cd–Sn–In

between 18 and 35 °C; (b) large latent heat of phase change; (c) little temperature difference between the melting point and the solidification point; (d) harmless to the environment; (e) low toxicity; (f) non-flammable; (g) stability for repetition of melting and solidification; (h) large thermal conductivity, for effective heat transfer; (i) ease of availability; (j) low price.

According to Table 6, paraffin is one of the ideal PCMs used in textiles. Paraffin has a high heat of fusion per unit weight, a wide range of melting points (−12 to 187 °C) and they are flammable, nontoxic, noncorrosive, chemically inert, stable below 500 °C, and predictable. They also possess properties of negligible super cooling, low volume change on melting, low vapor pressure in the melt, reasonable cost, and high wetting ability. Wang et al. studied the effect of paraffin wax in design of cold protective clothing [97]. The experimental results showed that the ear canal temperature when subjects wearing clothing treated with paraffin was significantly higher than that when subjects wearing moisture management clothing. Sánchez et al. also applied PRS® paraffin wax in textiles and successfully produced thermo-regulating textiles [98,99]. This kind of paraffin was a mixture of hydrocarbons C_{19}–C_{27} produced and commercialized by the petrochemical company Repsol YPF (Spain). Its energy storage capacity was 202.6 J/g with melting temperature range in 40–45 °C. Besides, due to the low melting point, paraffin needs to be microencapsulated so that the total phase change process can take place only in the capsules, avoiding dripping off the clothes when it melts. Therefore, microcapsule production is very important in PCM's practical applications. The microcapsule of PCM with walls less than 2 μm in thickness and 20–40 μm in diameter is useful when integrated in fabrics, as shown in Fig. 4 [100]. A relatively large surface area for heat transfer can be obtained when the capsule size is small. Therefore, the PCM can react to an external temperature change rapidly.

Taking factors such as cost, health and environment into consideration, a microencapsulation method based on a suspension free radical polymerization process for the encapsulation of PCMs was also used before, which was relatively inexpensive, simple and technically easy. PCMs such as hydrated inorganic salt and *n*-alkenes have been studied in recent years. Gao et al. carried out several studies on thermo-regulating application of a kind of certain salt mixtures [101,102]. The main ingredients include sodium sulfate and water (sodium sulfate decahydrate $Na_2SO_4 \cdot 10H_2O$, known as Glauber's salt), and additives. It is known that physical and chemical properties of Glauber's salts are very attractive for thermal storage: the salt has a convenient melting temperature (32.4 °C) and melting latent heat of 254 kJ/kg which gives high energy at its melting point [95]. Their research validated the practical cooling effect of hydrated inorganic salt on human subjects. Apart from hydrated inorganic salt, *n*-alkenes are also popular PCMs for textiles. Both pure compound and binary mixture of *n*-alkenes can be used as PCM materials [103,104]. Furthermore, it is worth noticing that the use of binary mixture allows to adjust the melting point or phase change point by modifying the composition which also leads to a decrease in the overall latent heat of fusion [103].

Compared with these conventional PCMs, room temperature liquid metal seems to meet most of the requirements for thermal comfort fields. For example, liquid gallium owns an perfect melting temperature about 29.77 °C, which is close to body temperature, a latent heat about 80.3 kJ/kg and a large thermal conductivity between 29.28 and 40.6 W(m °C). Besides, liquid gallium is non-flammable, low toxic and stable for repetition of melting and solidification. Owing to these advantages, we previously proposed a new type of composite fabric consisting of fiber yarn and gallium-based liquid metal, which proved good thermal conductivity, thermoregulation ability, and very nice electromagnetic shielding effect [105]. In brief, room temperature liquid metal opens enormous potential as a novel PCM that can be used in thermal comfort field.

3.3. PCM used in building heat storage

In recent years, PCMs used in building walls are drawing more and more attentions. The first published studies dealing with PCM integration into building walls can be traced back to the 1980s. Since then, the number of articles has increased significantly. Among them, it is worth noting that more than 17 percent of those articles were published by the authors from China [17]. This ratio suggests that since the 1980s, along with China's economy development and increasing living standard, the demand in thermal comfort of buildings also grows rapidly [106]. As is well known, thermal comfort of buildings is closely related to energy consumption. Integrating PCM into a building or building service systems is a practical way of promising potential to cutting down building energy consumption and enhancing indoor thermal comfort.

The cooling/heating function of PCM in buildings can be explained as follows. When ambient temperature rises, the chemical bonds of PCM will break up whereby the material will change from solid to liquid. The reaction is endothermic, and the PCM absorbs heat from indoor air. When ambient temperature falls again, liquid PCM will turn back to solid. The reaction is exothermic, and the PCM desorbs heat to indoor air. When the cycle continues, the indoor air temperature will be more stabilized in thermal comfort range. Fig. 5a shows the indoor and outdoor air temperatures for a building in a whole year when

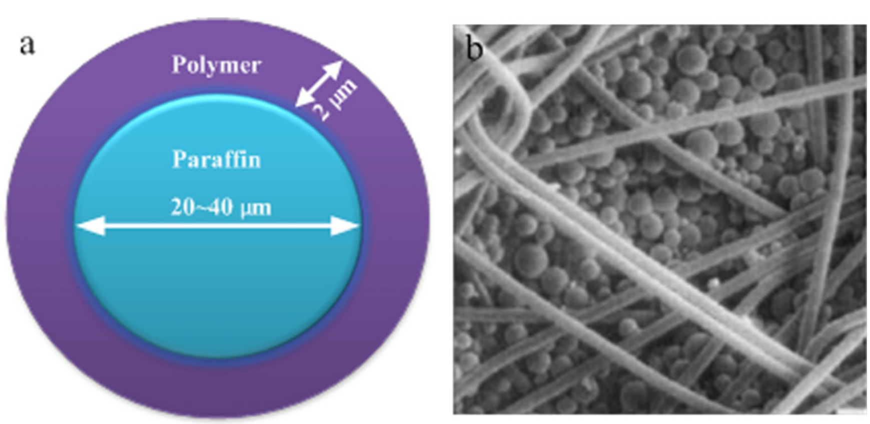


Fig. 4. Microcapsule: (a) Hard polymeric shell with paraffinic PCM core; (b) PCM microcapsules coated on fabric surface (with permission from Gordon [100]).

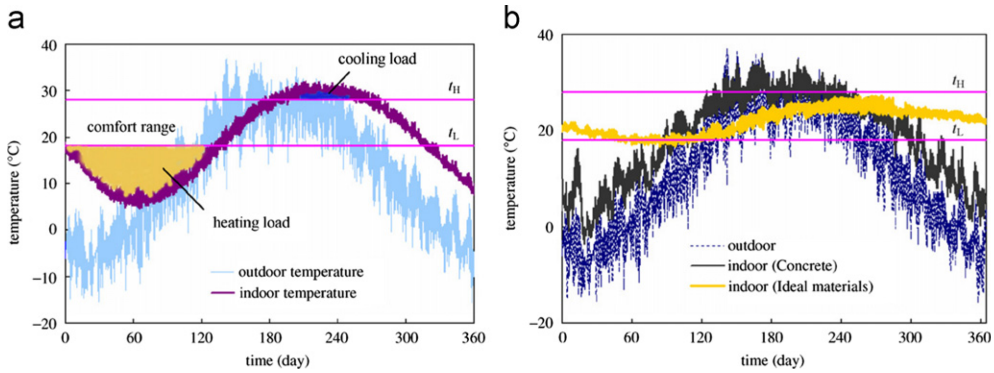


Fig. 5. (a) Indoor and outdoor temperature variation vs. time when there is no space heating and cooling and (b) indoor temperatures of a room applying concrete and ideal building materials (with permission from Zhang et al. [107]).

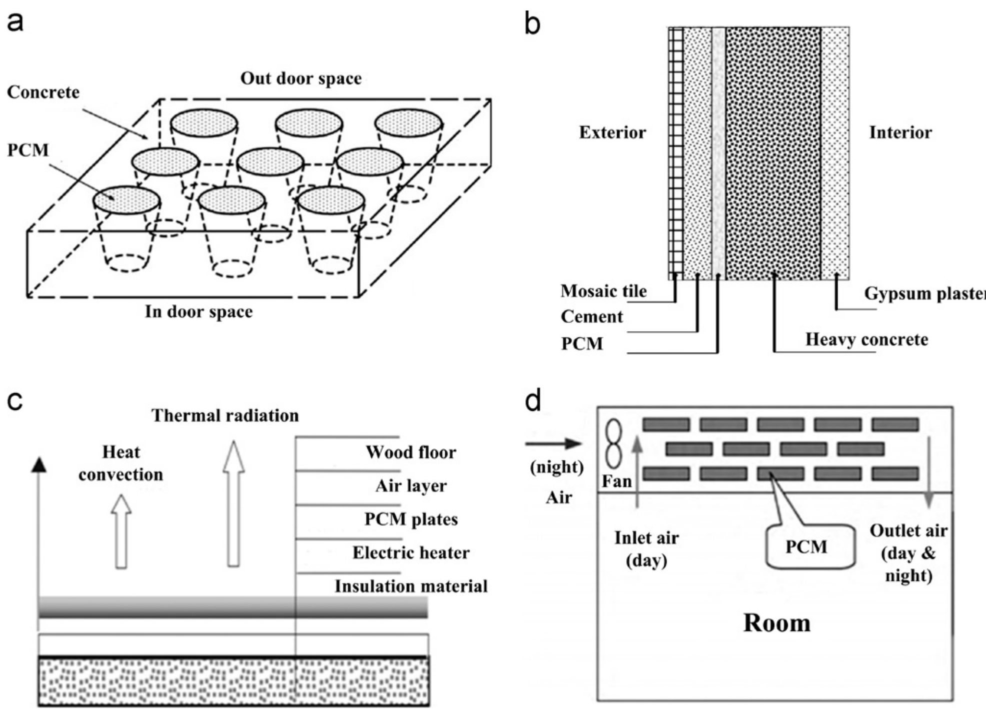


Fig. 6. (a) Schematic representation of the roof with holes filled with PCM; (b) Plane view and cross section of a typical residential flat; (c).Schematic of under-floor electric heating system with shape-stabilized PCM plates; (d) Schematic of the NVP system (with permissions from Alawadhi et al. [109], Chan [110], Lin et al. [111] and Kang et al. [112]).

there is no space heating and cooling. The heating and cooling load decrease with decreasing the temperature difference. Fig. 5b shows that PCMs can provide high latent heat thermal energy storage density over the narrow range of temperatures typically encountered in buildings. When PCM is cooperated in building, the indoor air temperature fluctuation in a day is decayed compared with environmental temperature. When outdoor temperature is seriously deviated from thermal comfort zone, the PCM will sustain the heating or cooling load.

PCMs can not only be integrated into building structures, but also cooling and heating systems or so-called latent heat thermal energy storage systems (LHTES). The application of PCMs in building structures currently focuses on several aspects: gypsum wallboards, concrete and insulation materials. These building materials are relatively more possible to be cooperated with PCMs due to their porous structures [108]. Alawadhi and Alqallaf performed a numerical study on a building roof with conical holes containing PCM, as shown in Fig. 6b. The results indicated that the heat flux at the indoor surface of the roof can be reduced up to 39% [109]. Chan designed a typical residential flat with PCM integrated external walls as shown in Fig. 6, which finally gave a comparatively higher decrease in the interior surface temperature up to a maximum of 4.14% and an annual energy saving of 2.9% in air-conditioning system [110].

The applications of PCMs in LHTES systems have two main aspects: floor electric heating combined with PCMs (FEHP) and night ventilation system with PCMs (NVP). As to the FEHP system, PCM layer is heated and melted by electric heaters by using cheaper night time electricity and the system stores heat. Then, during the day time the electric heaters are switched off and the PCM layer solidifies, discharging the heat stored at night to the indoor room air. This will provide a significant economic benefit due to the different electricity tariffs for peak periods at day and off-peak periods at night. The schematic view of a typical FEHP system designed by Lin et al. is shown in Fig. 6c, the PCM plates in the floor acted as the latent heat container [111]. As to NVP system, Fig. 6d shows a NVP cooling system proposed by Kang et al. [112]. At night, the outdoor cool air is blown through the

NVP system to charge cool to the PCM array. In the day, air cycles between the NVP system and the room, and the cool stored by the PCM array at night is discharged to the room air. Arkar et al. also presented a novel NVP system consisted of a cylindrical PCM device and a mechanical ventilation system, as shown in Fig. 7a. [113]. The ventilation system with PCM spheres were studied in the case-study low-energy single-family building, as reflected by Fig. 7b. They found that the NVP system with 6.4 kg of PCM per square meter of floor area is the optimum for the free cooling of the case-study building. To conclude, utilizing LHTES systems as above in buildings is an economical passive cooling way to keep the indoor air temperature comfortable.

PCMs that can be applied in buildings have a suitable transition temperature point or range, generally between 18 °C and 28 °C, which is also the human comfort temperature zone. PCMs used in building wall applications can be either organic materials or inorganic materials. The advantages and disadvantages are comprehensively discussed in [17,114]. Up to now, several PCMs that have been applied in building envelop are listed in Table 7 [115–117].

It is worth to point out that, organic PCMs like paraffins and fatty acids have no evident supercooling or phase segregation compared to inorganic materials like salt hydrates. When phase change occurs, inorganic PCMs have a tendency to supercool. The components of inorganic PCM will not melt congruently and thus segregation occurs. Supercooling and phase separation of inorganic PCMs often weaken the thermal behavior of PCMs. When the phase-change cycles repeated a number of times, the transition zone of the inorganic PCM will drift progressively. Moreover, when contacted with inorganic PCMs, corrosion of metals occurs, as Fig. 8a indicates. Thus, the corrosion effects will finally weaken the stability and reliability of building's metal structures. From this point of view, the organic PCMs seem to be more suitable for buildings. However, the fire proof performance of PCMs should also be taken into

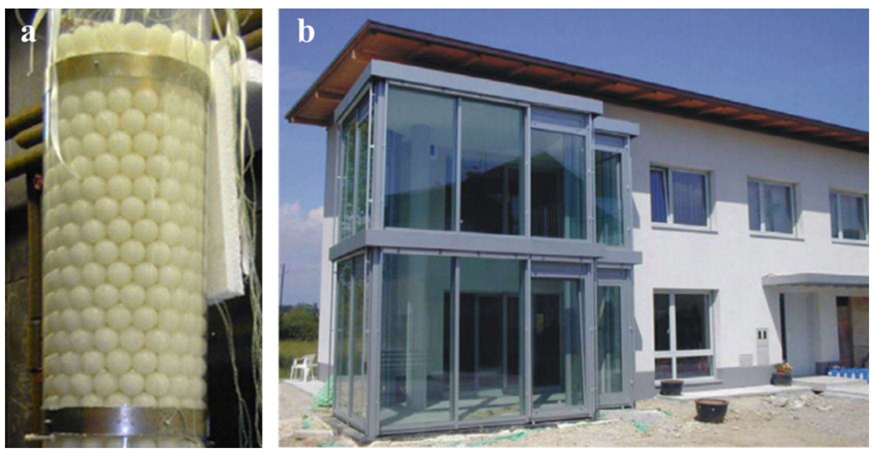


Fig. 7. (a) Cylindrical PCM device; (b) Low-energy single-family building (with permission from Arkar and Medved [113]).

Table 7
Several PCMs applied in building envelop [115–117] and their thermo-physical properties for comfort applications.

PCM	Type	Transition point/range(°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/(m °C))
Butyl stearate	organic	18–23	123–200	0.21
Black paraffin	organic	25–30	150	–
Capric–lauric45/55	Fatty acid mixture	21	143	–
Capric–lauric82/18	Fatty acid mixture	19.1–20.4	147	–
Capric–lauric61.5/38.5	Fatty acid mixture	19.1	132	–
Capric–myrstic73.5/26.5	Fatty acid mixture	21.4	152	–
Capric–palmitate75.2/24.8	Fatty acid mixture	22.1	153	–
Capric–stearate86.6/13.4	Fatty acid mixture	26.8	160	–
Capric–lauric45/55	Fatty acid mixture	21	143	–
Capric–lauric82/18	Fatty acid mixture	19.1–20.4	147	–
$CaCl_2 \cdot 6H_2O$	Inorganic	24–29	192	0.54–1.088
$CaCl_2 \cdot 6H_2O + Nucleator + MgCl_2 \cdot 6H_2O$ (2:1)	Inorganic	23	–	–
$CaCl_2 \cdot 6H_2O$ 66.6%+33.3%$MgCl_2 \cdot 6H_2O$	Inorganic	25	127	–
$CaCl_2$ 48%+NaCl 4.3%+KCl 0.4%+H_2O 47.3%	Inorganic	26.8	188	–
Climsel C_{24}	Inorganic(salt hydrate)	24	108	1.48
$FeBr_3 \cdot 6H_2O$	Inorganic(salt hydrate)	21	105	–
Hexadecane	Organic	180	236	–
$LiNO_3 \cdot 3H_2O$	inorganic(salt hydrate)	30	296	–
$Mn(NO_3) \cdot 6H_2O$	Inorganic (salt hydrate)	25.5 25.8	125.9 125.9–148	–
n-Heptadecane	Organic	19	240	0.21
n-Octadecane	Organic	28	200	0.148(liquid) 0.658(solid)
Polyglycol E600	Organic	22	127.2	0.8196(liquid,38.6 °C)
Paraffin C_{13}–C_{24}	Organic	22–24	189	0.21(liquid)
Paraffin C_{18}	Organic	27.5–22.5	244–243.5	0.148(liquid) 0.15(solid)

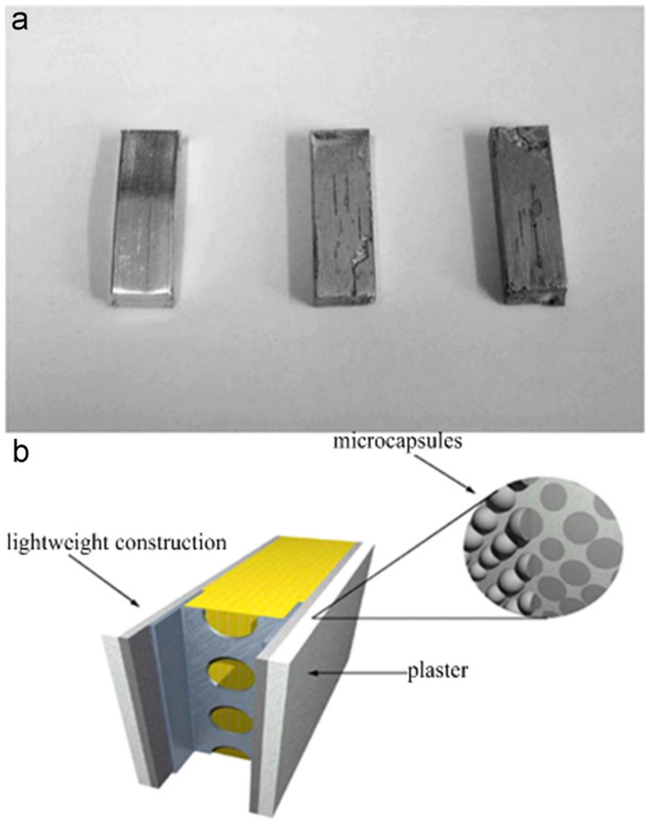


Fig. 8. (a) Aluminum treated with a salt hydrate: from left to right—before treatment, after treatment, and after treatment in contact with graphite (with permission from Mehling and Cabeza [118]) and (b) Schematic view of the PCM microcapsules are integrated into the interior plaster (with permission from Tyagi et al. [31]).

consideration. Most organic PCMs are flammable, which pose a serious potential danger of fire. Besides, organic PCM's thermal conductivity is also much less than inorganic PCM's [107,117]. Therefore, in order to compensate the low thermal conductivity of organic PCMs, heat transfer enhancement techniques should be adopted, including introduction of fins, inserting the metal matrix in PCM, PCM packed with Lessing rings, introduction of graphite in PCM base material in fibrous form and shape stabilized form and use of heat pipes [117].

In brief, all of the shortages of organic and inorganic PCMs applied in buildings can be summarized as having supercooling, phase separation, corrosion, flammability and low thermal conductivity. In this side, low melting point liquid metal owns moderated supercooling, no phase separation and none-flammability. Especially, its thermal conductivity is much larger than the above conventional PCMs. Therefore no more heat transfer enhancement techniques are needed. However, the corrosion effects of liquid metal with building structures might still exist. Our previous work has already investigated the corrosion effect of liquid gallium with four different types of metal substrates, which proved that materials like T2 Copper-Alloy, Anodic Coloring 6063 Aluminum-Alloy, and the 1Cr18Ni9 Stainless Steel present no evident corrosion signs in nearly five hours at 120 °C [119]. More detailed investigation should focus on the corrosion effects between different liquid metal and building structures.

Furthermore, from a practical point of view, most PCMs practically used in building envelope are solid–liquid PCMs. Because of the leakage issues, conventional solid–liquid PCMs remains difficult to be used in building envelop. To solve this problem, micro-encapsulation technology has been proposed to produce PCM micro-capsules used in buildings [114].

3.4. PCM used in thermal management on electronic devices

In recent years, PCMs have been widely used as an alternative cooling method for various applications such as spacecraft and avionics thermal control, personal computing and communication equipment, wearable computers, power electronic equipment, and portable phones etc. Passive thermal management scheme of PCMs can be used in the situations where heat dissipation is periodic or sudden transient. The selected PCM should have melting temperature below the device's maximum operating temperature, a large latent heat of fusion per unit mass, a high thermal conductivity, a strong specific heat and a small volume change on phase change. A kind of mixed radiator-fan was proposed, which contain the fins and PCM confined in the container. During the experiment, different PCM such as Eicosane, Heneicosane, SuntechP116 and Bi/Pb/Sn/Cd/In alloy were tested to investigate the cooling effect [120]. To evaluate the thermal characteristics of a PCM-based heat sink which can be potentially used for cooling of mobile electronic devices such as personal digital assistants (PDAs) and notebooks, a numerical study is conducted. The heat sink consists of a conventional, extruded aluminum sink embedded with appropriate PCMs. Some important parameters, such as PCM volume fraction, temperature difference, aspect ratio, and PCM properties, were studied to evaluate their effects on the thermal performance of the hybrid cooling system [121]. As we know that the mobile electronic device is used in moving condition, so the effect of the orientation must be examined before such hybrid cooling systems was practically used. Thus Wang et al. solved the two dimensional set of conservation equations to study the effect of the heat sink orientation on the thermal performance of a PCM-based cooling system [122]. In order to deal with the thermal issue occurred on mobile electronics, Kandasamy et al. investigated the feasibility of using PCMs in thermal control of portable electronic devices which are used intermittently [123]. The heat transfer characteristics of a PCM-based control unit were tested experimentally for various power input levels, orientations of the PCM package, and various melting/freezing times under cyclic steady state conditions. A flat quad PCM package was fabricated for this purpose. Furthermore, a generalized two-dimensional computational model is developed to assess the heat transfer performance of the PCM package.

Giovanni et al. conducted an experiment, in which, to prevent natural convection in the liquid phase, a solid slab of noctadecane (n-$C_{18}H_{38}$) was placed horizontally and the heat transfer was directed vertically downward to investigate the steady periodic solid–liquid phase-change heat transfer [124]. The side wall was insulated. During the evolution of the process, the temperature inside the octadecane was measured by thermocouples and numerically analyzed by control volume method. In order to examine the cooling effect on mobile phones using PCM, experimental prototypes of mobile phones were fabricated using aluminum heat sinks with different numbers of fins filled with n-eicosane. The devices were subjected to steady-state and transient charging and discharging at different power settings. It was found that the PCM melting rate increased with the power increased. The internal fins also helped to reduce the maximum device temperature. These findings indicated that the use of PCM based heat sinks were effective for the cooling of mobile phones under intermittent moderate usage conditions [125]. In Yang and Wang's study [126], a numerical investigation of transient three dimensional heat transfers was carried out with a hybrid heat sink to cool an electronic device. Remarkable heat transfer and

cooling characteristics were found with various power levels and orientations. The results indicated that the use of PCM in the aluminum hybrid heat sink would guarantee electronic packages' working at stable operation temperature. The test of orientation expressed the limited effect on the phase change performance of the system. The maximum temperature of the hybrid heat sink using *n*-eicosane can be well controlled bellow 47 °C. The local transient temperature was verified with experimental data reported in the literature. The thermal performance of PCM on a Ni-plated has been tested for the case that it was applied as a thermal interface material. The features of the PCM conformed to metal surfaces and heat transfer mechanisms were also explained [127]. Heat spreader for electronics cooling with PCM was investigated by means of simple computational approach. Here PCM was confined inside the thin walled pipes which work as fins. Such design provided better performance in both normal regimes of electronic cooling and in case of variable heat loads of radiator. Because of the high heat transfer surface area and specific air flow over pipes, heat spreaders of such type could keep microchip's temperature below 50 °C. Simultaneously, due to the PCM included inside the pipes, the heat spreaders were able to prevent microprocessor from overheating in case of transient heat load. And in case of accidental fan failure, they can substantially slow down the rise of temperature transitorily. Such a good features in unsteady states were achieved with relatively small amount of PCM. However, the heat dissipation to the PCM was very efficient and nearly whole amount of PCM absorbed excess heat immediately after thermal disturbance. The schematic was depicted in Fig. 9 [128].

Also in order to reduce the rising of the junction temperatures due to thermal transient effects, Lu et al. has tested the high power electronic packages with phase change cooling [129]. Kandasamy et al. investigated the feasibility of PCM-based heat sinks used in thermal management of transient electronic devices experimentally and numerically. The heat transfer features of the PCM-based heat sink fixed on a quad flat package electronic device were studied experimentally and the results were compared with that of a pure heat sink without embedded PCMs. Specified local temperature inside the PCMs and the die junction temperature were measured [130]. Fig. 10 presents the cross-sectional schematic of PCM filled heat sink with plastic quad flat package.

Alawadhi et al. investigated the cooling effectiveness of a thermal control unit (TCU) for portable electronic devices, which the TCU was composed by an organic PCM and a thermal conductivity enhancer (TCE). The TCU was effective in thermal management of electronic devices especially their operating time was limited to a few hours. To overcome the low thermal conductivity of the PCM, a TCE was inserted into the PCM to increase its conductivity. A numerical model was then used to improve the experiment [131]. Fok et al. have studied the effects of a PCM in heat sinks (with and without internal fins) on the cooling of portable hand-held electronic devices with input power ranging from 3 to 5 W experimentally [132]. This is an extension of the work of Tan and Tso [133], in which the transient thermal performances of the heat sinks were investigated under frequent, heavy and light usage conditions. The feasibility of transient thermal management of mobile phones using PCMs was experimentally investigated by Hodes et al. [134]. At selected intervals of using time, the non-uniform cover temperature field of the mobile phone was displayed by an infrared (IR) camera, meanwhile the temperatures of both PCM and simulated heater were measured by thermocouples. Also other experiments were carried out to observe the temperature rise of the junction temperatures, in which four heaters were placed on the top of heat storage unit (HSU) filled with n-eicosane, as illustrated in Fig. 11. The HSU was used to stabilize the system temperature at an allowable working range below 50 °C. In contrast, the junction temperature exceeded the working temperature at high power dissipation that meant the junction temperature increased rapidly without the PCM in HSU.

In consideration of the inconvenience of the liquid state PCM, Wirtz et al. investigated the so called dry PCM, which belongs to the solid–solid PCM [135]. In their work, they evaluated the thermal response characteristics of a hybrid cooler charged with the dry phase change compound. A mathematical model that simulated the effect of a cooler heat storage unit was formulated and used to evaluate different electronics cooling strategies. A prototype heat sink was tested, and used to validate the

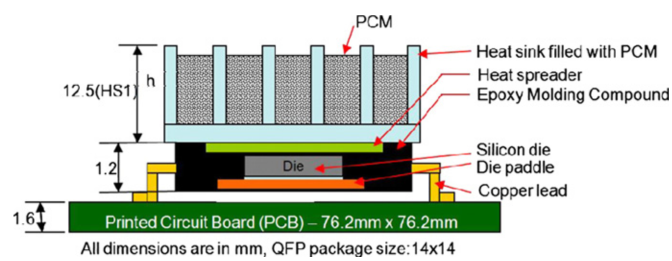


Fig. 10. Cross-sectional schematic of PCM filled heat sink with plastic quad flat package (QFP) (with permission from Kandasamy et al. [130]).

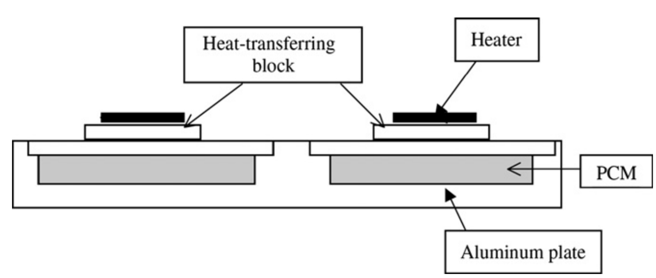


Fig. 11. Heat storage unit (HSU) containing the PCM (with permission from Tan and Tso [133]).

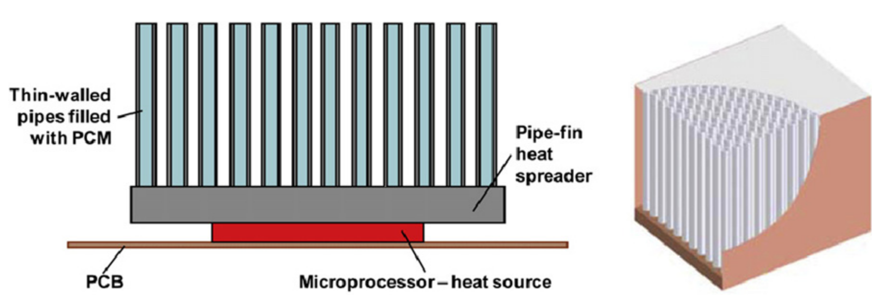


Fig. 9. Heat spreader for electronics cooling with pipe-fins filled with PCM (with permission from Jaworski [128]).

Table 8
Corresponding PCM candidates and their thermo-physical property.

PCM	Solid state			Phase change		Liquid state		
	Density (kg/m^3)	Specific heat (kJ(kg °C))	Thermal conductivity (W(m °C))	Enthalpy of fusion (kJ/kg)	Melting point (°C)	Density (kg/m)	Specific heat (kJ(kg °C))	Thermal conductivity (W(m °C))
Gallium [138,139]	5910	0.374	40.6	80.12	29.8	5904	0.373	29.28
$Na_2SO_4 \cdot 10H_2O$ [61,140]	1485	1.76	0.544	251.2	32.4	1458	3.3	0.544
N-eicosane [132,141]	788	2.46	0.15	247	36.8	788	2.46	0.15
Paraffin [130,137,142]	910	2.51	0.21	189	40–43	765	2.21	0.29

mathematical model. Su and Liu has developed a novel polymeric solid–solid phase change heat storage material, which called polyurethane block copolymer structure (PUPCM) composed of high molecule weight polyethylene glycol (PEG) as soft segment, 40-diphenylmethane dissyanate(MDI) and 1, 4-butanediol (BDO) as a chain extender. DSC, POM, SEM and WAXD tests were performed to investigate the phase transition behaviors and crystalline morphology. The results indicated that the PUPCM showed typical solid–solid phase transition properties, e.g. suitable transition temperature, high transition enthalpy and good thermal stability [136].

So far, many conventional PCMs have been investigated and used in thermal management of the electronic devices. However, a variety of troubles occurred during the working, such as the low thermal conductivity, the small latent heat, the bulky pattern, and so on. Clearly, the low melting point liquid metal used as PCM can well settle the above problems. Some essential features for an appropriate room temperature PCM used in thermal management of the eletronic device can be summarized as: (i) Low melting point. (ii) Large specific heat per unit volume in both liquid and solid state. (iii) Large enthalpy of fusion per unit volume. (iv) High thermal conductivity in both liquid and solid state. (v) Friendly to human and environment [137].

In order to balance metal PCM with traditional PCMs, several corresponding PCM candidates were listed in Table 8. Here sodium sulfate decahydrate delegates the inorganic PCMs, N-eicosane stands for the organic PCMs, and the paraffin is the most used PCM. Compared with them, the gallium was found to present a lot of advantages as PCM such as: (i) The thermal conductivity of gallium is considerably larger than that of other PCM candidates in Table 8, which would enhance the heat transfer and thus reinforce heat dissipation to the environment. (ii) Based on Table 8, one can calculate that the specific heat per unit volume of the PCMs were 473509.2 kJ/m^3 for gallium, 373032 kJ/m^3 for $Na_2SO_4 \cdot 10H_2O$, 194,636 kJ/m^3 for *N*-eicosane and 183,330 kJ/m^3 for paraffin, with gallium as the largest. This will prolong the temperature holding time during working of the electronic device. (iii) The specific volumetric dilatation during phase change of gallium was relatively small, which was not listed in Table 8.

4. Emerging scientific issues and technical challenges

Though low melting point metals or alloy have many advantages as discussed, there still exist some emerging scientific issues and technical challenges waiting for solving such as:

(i) The usable melting point of nontoxic metal or metal alloy is 8–30 °C for gallium and gallium-based alloy, and 40–100 °C for Bi-based metal alloy. The nontoxic metal or metal alloy with melting point below 8 °C or between 30–40 °C has yet to be discovered until now.
(ii) Even for the metal and metal alloys which have determinate melting point, their thermo-physical properties such as density, thermal conductivity, specific heat at solid or liquid state, latent heat or the expansion coefficient, are sometimes conflicting and confusing in existing literature, calling the establishment of unified and reliable database.
(iii) In view of the possible corrosion of liquid metal to some structure material, the compatibility and stability between metal and the container to hold the metal PCM need further study.
(iv) The supercooling as widely existing in metal and metal alloy affects the performance of phase change from liquid to solid. In order to reduce the supercooling degree, nucleating agent could be loaded to the metal and metal alloy, e.g. adding SiO_2 into gallium. Nucleating agents applying to different metal and metal alloys need to be explored further.
(v) The high price limited the application of gallium alloys on a large scale. Therefore, more efficient way to utilize these metals should be taken into serious account, such as making PCM composite containing both conventional PCMs and metal PCMs. Besides, additional low melting point metals or alloys should also be explored.

In order to guarantee the safety and stability of the PCM system [143], a critical technical issue was the selection of container material. Several basic features for the container material include: intensity, flexibility, thermostability, diathermancy, environmental adaption to maintain system sealed well. Most important of all, the PCM must not corrode with and permeate though the container material. The chemical reaction between PCM and container should be avoided. Further, stretch materials which satisfy the requirement were favored for their volume change with the PCM expanding and shrinking.

5. Conclusion

In this day and age, power shortage and unstable power supply remain serious challenge. The main role of PCEST is to reduce the time or rate mismatch between energy supply and energy demand. However, the currently available PCEST still presents in most cases an insufficient energy density, limited efficiency and reliability. These issues would restrict its broad range of applications. Overall, the conventional PCMs still request serious innovations due to their intrinsic shortcomings in the thermal management of electronic device and temperature regulation in green building.

The newly emerging low melting point metal or alloy as PCM is inherited with several outstanding merits: (1) large conductivity,

which is beneficial in enhancing heat transfer performance within the system; (2) large volumetric enthalpy of fusion and specific heat, which would improve the compactness and thermal storage capability of the system, (3) long term stability after millions of solidifying and melting process. Such material offers rapid response and quick heat absorption with small volume expansibility, which ensures its significant feature as PCM. Due to the relatively large latent heat per unit volume and large density, it is especially suitable for the restricted heat dissipation space, within which the metal PCM can absorb large amount of heat efficiently. As a smart material for automatic thermal management, the low melting point metal or alloy based PCM still requests tremendous efforts to clarify the fundamental phase change mechanisms as well as practical issues thus involved. Besides, guaranteeing the compatibility between such PCM and the container is very necessary. As has been revealed in our former experiments, the liquid gallium will corrode some metals such as aluminum and copper. This may lead to fatal failure of the thermal management. Therefore, to prevent such things to occur, specific surface coating on the substrate material is critically needed or different container materials can be selectively adopted. Further, certain measures such as microencapsulated metal PCM [144] should also be explored. Overall, the former contributions from the conventional PCM will shed light on developing future low melting point metal based PCM technology.

In summary, the metals and alloys with melting point between at 0 °C and 100 °C are showing increasing potentials in various thermal and energy management fields, especially for those situations where the cooling space was strictly limited and the heat source works inconsecutively. Giving the fact the fundamental properties and applications of such metal based PCMs were significantly ignored in the past few decades, it is reasonable to believe that a fruitful progress along this direction will come true in the near future. The present work will arouse attentions from both academic and industrial areas, which may then further promote intensive research and application in the area.

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